III.A.15 Combined Theoretical and Experimental Investigation and Design of H_2S Tolerant Anode for Solid Oxide Fuel Cells

Objectives

- Investigate the mechanism for deterioration of solid oxide fuel cell (SOFC) anodes operating at the H_2: H_2S: CO ratios found in coal syngas.
- Molecular modeling of the anode materials interacting with chemical species.
- Validate the theoretical model with experimental data.

Accomplishments

- Established the detrimental influence of H_2S on H_2 oxidation at anode material from quantum chemistry calculations; binding energy for H_2 was reduced from -80.1 kcal/mol to -21.6 kcal/mol in the presence of H_2S gas molecules.
- Molecular dynamics calculations confirm that H_2S gas molecules slow the diffusion of H_2 molecules towards anode material.
- Analyzed the impact of CO on the mixture of H_2 and H_2S; CO decreased the diffusion coefficient of H_2S.

Introduction

Coal syngas is the gas produced from the burning of coal and has a good amount of hydrogen along with other chemical species as such as CO and CO_2. However, coal syngas also contains H_2S at high concentrations between 0.5-5% depending on where the coal is mined [1]. Of the different types of fuel cell, the solid oxide fuel cell (SOFC) is the most viable option to use coal syngas as its fuel supply because it operates at 850-1000°C. It is also known that SOFCs can handle CO and CO_2 as contaminants in the H_2 supply because of its high operating temperature. But the presence of H_2S in the fuel stream will deteriorate the anode material. Most of the research has been focused on developing new anode materials for SOFCs rather than studying the cause of the anode deterioration due to H_2S. In this project, we propose to use a systematic approach to understanding the effect of H_2S from syngas on the anode materials (Ni-YSZ, Ni-CeO_2-YSZ) with molecular modeling computations, and to perform experiments to validate the models.

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Approach

In this study, molecular modeling is used to understand the interaction of H_2S with anode materials (Ni-YSZ, Ni-CeO_2-YSZ). Molecular modeling consists of first principle quantum chemistry (QC) calculations using Gaussian 03 software to optimize the structure of each compound and the systems consisting of anode and different chemical species. Physical properties, such as diffusion coefficient of the chemical species and their interactions with anode material, are calculated using molecular dynamics (MD) simulations with Cerius2 (v 4.8) software. Finally, an experimental set-up will be constructed to perform SOFC experiments with different anode materials and validate the mathematical models.

Results

Molecular modeling of different SOFC anode material chemical species was studied. First, the electrolyte of SOFC, yttria-stabilized zirconia (YSZ), was optimized by QC calculations using Gaussian 03 software. NiO was added to the optimized YSZ structure to form Ni-YSZ, the anode material. All the possible systems consisting of Ni-YSZ (anode), H_2, H_2S and CO were constructed and quantum calculations were performed. The binding energies for each system are shown in Table 1. The binding energy for each system has a negative value which means the oxidation of the components on the Ni-YSZ surface is thermodynamically feasible. In case of single molecules, oxidation of H_2 is favored more than oxidation of H_2S and CO because the binding energy for H_2 (-80.1 kcal/mol) is lower than H_2S (-21.4 kcal/mol) and CO (-23.9 kcal/mol).

The binding energy for the system where H_2S is combined with H_2 (-21.6 kcal/mol) is higher than the system with only H_2, which means H_2 oxidation on the Ni-YSZ surface is obstructed by the presence of H_2S molecules. But when CO is mixed with H_2, the binding

TABLE 1. Binding Energies for Various Combinations of Gas Components

Systems	Binding Energy (kcal/mol)
H_2	-80.1
H_2S	-21.4
CO	-23.9
$H_2 + H_2S$	-21.6
H_2 + CO	-155.5
H_2S + CO	-134.6

energy (-155.5 kcal/mol) is far less than the binding energy for the CO+H_2S system (-134.6 kcal/mol), which suggests that oxidation of both CO and H_2 on the surface of Ni-YSZ anode is more favored than the CO+H_2S system.

The computational chemistry model was extended and MD calculations were performed to understand the interactions between the atoms in the anode and the chemical species (H_2, H_2S and CO) in its environment. The radial distribution function (RDF) was used to determine the packing and orientation of the chemical species and anode material. The RDF plot gives the interaction of each chemical species with different atoms in the anode as a function of distance from the surface of the anode.

One of the RDF plots for the H_2 system at 25°C showed that H_2 has a higher affinity for the Ni atom in the anode than other atoms (Y, Zr and O), which means H_2 oxidizes at Ni sites in the Ni-YSZ anode. Figure 1 shows the RDF plot for the Ni-H_2 pair at 850°C in the presence of H_2S and CO molecules. The pure H_2 system has the highest peak value, which decreases with the addition of H_2S and CO to the mixture. This proves again that oxidation of H_2 at Ni sites are slowed down by the presence of H_2S and CO molecules. In addition, one can observe the position of the Ni-S pair from the H_2/H_2S system, which is farther away from the anode surface as compared to the Ni-H_2 pair. This confirms that H_2 is more likely to get oxidized at Ni sites than the H_2S molecule. Interaction of H_2S with different atoms in the anode and H_2 molecules at 850°C is shown in Figure 2. The RDF plot shows that S forms a pair with Ni and H_2 rather than with any other atoms. The Ni-S pair is slightly farther away from the anode than the Ni-H_2 pair.

Other than the RDF plot, MD calculations can be used to find the diffusion coefficient of each gas molecule. In Table 2 the diffusion coefficients for H_2, H_2S and CO in various systems are listed. Diffusivity for pure H_2 was found to be 1.35 x 10^{-4} cm^2/s, but when H_2S gas was mixed with H_2, the diffusion coefficient of H_2 was lowered by 20% to 1 x 10^{-4} cm^2/s. This observation agrees with QC calculations that in a H_2+H_2S mixture, oxidation of H_2 takes place at a slower pace due to transport limitations. Now with the addition of CO to H_2 gas, the H_2 diffusivity has been dropped to 5 x 10^{-6} cm^2/s, which is 96% lower than the pure H_2 system. In the case of a H_2+H_2S(2%)+CO(2%) mixture, CO slows down both the diffusion of H_2 (9 x 10^{-6} cm^2/s) and also H_2S (2 x 10^{-9} cm^2/s).

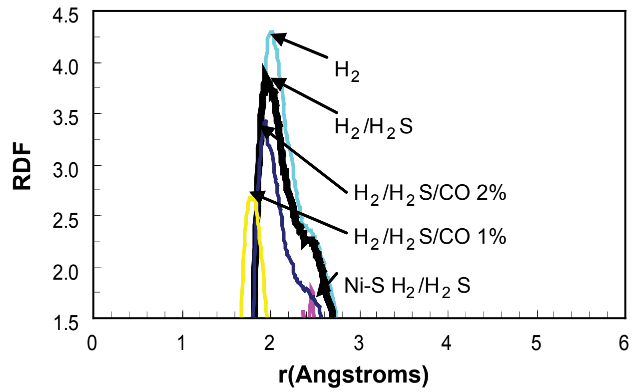

FIGURE 1. RDF Plot for Ni-H_2 Pair at 850°C with the Presence of H_2S and CO

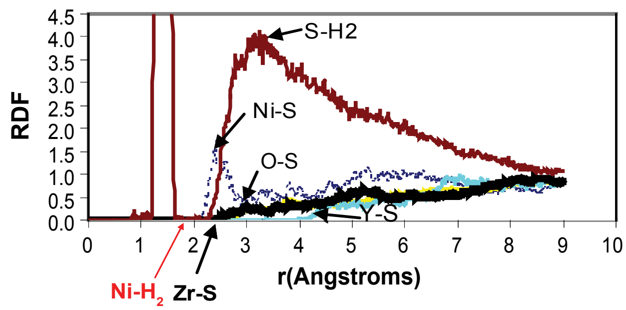

FIGURE 2. Interaction of H_2S Molecule with Ni, Y, O, Zr Atoms and H_2 Molecule at 850°

TABLE 2. Diffusivities of the Gas Components at 850° C for Different Systems

Systems	H_2 Diffusivity (cm^2/s)	H_2S Diffusivity (cm^2/s)	CO Diffusivity (cm^2/s)
H_2	1.35 x 10^{-4}	–	–
H_2 + H_2S (2%)	1 x 10^{-4}	1 x 10^{-5}	–
H_2 + CO (2%)	5 x 10^{-6}	–	3 x 10^{-7}
H_2 + H_2S (1%) + CO (1%)	2 x 10^{-5}	8 x 10^{-9}	6 x 10^{-9}
H_2 + H_2S (2%) + CO (2%)	9 x 10^{-6}	2 x 10^{-9}	6 x 10^{-9}

Conclusions and Future Directions

- Quantum chemistry calculation proves oxidation of pure H_2 is more thermodynamically favored on the Ni-YSZ surface than pure H_2S and CO.
- RDF plots for H_2 indicate that H_2 has a greater affinity for the Ni atom than any other atoms in the anode material.
- Diffusion of H_2 was slowed down in the presence of H_2S and CO, but when all the three gases are mixed, CO reduces the diffusion coefficient of H_2S.
- In the future, we would like to include N_2 and H_2O (moisture) atoms to the anode environment and perform QC and MD calculations.
- Perform molecular modeling with another anode material – Ni-CeO_2-YSZ.
- Design and construct a SOFC experimental set-up to verify the theoretical model.

FY 2006 Publications/Presentations

1. "Theoretical Investigation of NiYSZ in the Presence of H_2S" Marquez, A., De Abreu, Y., and Botte, G. G., *Electrochemical and Solid-State Letters*, 9 (**3**) A163-A166 (2006).

2. "Theoretical Investigations of Solid Oxide Fuel Cell Anode Materials" AIChE 2005 Annual Meeting, October 30th – November 4th, 2005, Cincinnati, OH.

3. "Theoretical Investigations of Solid Oxide Fuel Cell Anode Materials in the Presence of H_2/H_2S/CO" The 31st International Technical Conference on Coal Utilization & Fuel Systems, The Clearwater Coal Conference, May 21-25, 2006, Clearwater, FL.

References

1. G. Y. Lai, *High Temperature Corrosion of Engineering Alloys*, ASM International, Materials Park, OH (1990) p. 117.